IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re application of	)	
	)	
R.Terry K. Baker et al.	)	Art Unit 1754
	)	
Serial No. 09/902,113	)	Before the Examiner
	)	
Filed: July 10, 2001	)	Stuart L. Hendrickson
	)	

CRYSTALLINE GRAPHITE NANOFIBERS
AND A PROCESS FOR PRODUCING SAME

Honorable Assistant Commissioner of Patents
Alexandria, VA 22313-1450

DECLARATION UNDER 35 U.S.C. 1.132

R. Terry K. Baker declares and says:

That he is a named inventor on the instant application.

That he has read and understands the Office Action dated February 25, 2004.

That he has read and understands the Audier et al. reference that teaches the formation of 3-D "tubes" from the decomposition of CO over Fe-Ni (25:75) and Fe-Co (50:50) alloys at temperatures from 550° to 600°C, respectively.

That he has had the following experiments conducted under his supervision which show that the presence of hydrogen with CO is critical for the production of the instantly claimed graphite nanostructures. This data also shows that it is unexpected that only a very specific catalyst, in combination with both carbon monoxide and hydrogen, within a very narrow temperature window is able to produce the so-called "ribbon" and "multifaceted tubular" graphitic nanostructures that are instantly claimed.

Fe-Ni with CO and CO/H_2

Table 1 shows the yields of solid carbon (expressed as grams of carbon/grams of catalyst) for the reaction of various Fe-Ni alloys with CO and CO/H_2 mixtures at 600°C. When the corresponding reactions were performed at 550°C the overall amounts of solid carbon were substantially decreased, however, the relative yields were about the same as those presented in Table 1.

TABLE 1

Catalyst	CO	CO/H_2 (4:1)	CO/H_2 (2:1)	CO/H_2 (1:1)	CO/H_2 (1:4)
Fe-Ni (6:4)	2	32	28	18	11
Fe-Ni (4:6)	1.5	18	27	24	12
Fe-Ni (1:3)	1.2	4	5	4	2

TEM examination of the solid carbon deposits showed evidence of major differences in the structural characteristics as a function of Fe-Ni alloy composition and CO with and without added hydrogen. All Fe-Ni alloys produced very small amounts of nanotubes from pure CO at 550°C. It was found that although these nanotube structures had their graphite planes aligned in a direction parallel to the fiber axis, the resulting structure was cylindrical. These characteristics are similar to the "fibrils" produced by Tennent, US 4,663,230, from the interaction of supported Fe catalysts with various carbon-containing gases in the absence of added hydrogen.

When the same set of Fe-Ni alloys were reacted with CO/H_2 mixtures at temperatures ranging from 550 to 600°C, distinct differences in the structural characteristics were observed. The nanofibers produced from a Fe-Ni (6:4) catalyst with CO/H_2 was found to have a structure in which the graphite sheets (platelets) were aligned substantially parallel to the longitudinal nanofiber axis and which had a multi-faceted cross-sectional geometry (A nanostructure of the instant invention). On the other hand, the nanofibers produced from the Fe-Ni (4:6) catalyzed decomposition of CO/H_2 took the form of a mixture of nanofibers in which the graphite sheets were oriented substantially perpendicular to the fiber axis in a so-called "platelet" morphology, whereas other structures adopted a spiral growth form. In sharp contrast, the Fe-Ni (1:3) catalyst

did not generate carbon nanotubes under these conditions, but instead tended to form "shell type" structures, consistent with the disclosure of Audier et al.

Co-Fe (1:1) with CO and CO/H_2

TEM examination showed that the solid carbon produced when Co:Fe (1:1) was heated in CO and CO/H_2 mixtures at temperatures ranging from 500 to 600°C were the same. In the presence of H_2, however, the amounts of material were increased significantly. There was evidence of two types of products, one in which many nanofibers grew from a single catalyst particle in a so-called "octopus" arrangement and a smaller fraction of cylindrical tubular fibers that did display an ordered crystallographic arrangement that one normally associates with carbon nanotubes. No nanostructures as instantly claimed were produced.

Fe with CO and CO/H_2

Table 2, below, shows the yields of solid carbon (expressed as grams of carbon/grams of catalyst) for the reaction of powdered Fe with CO and CO/H_2 mixtures at 600°C.

TABLE 2

Catalyst	CO	CO/H_2 (4:1)	CO/H_2 (2:1)	CO/H_2 (1:1)	CO/H_2 (1:4)
Fe	0.5	22	23	25	26

TEM examination of the solid carbon produced from the interaction of pure Fe with CO alone showed that it was comprised of graphite shells with some amorphous types of carbon nanofibers. On the other hand, examination of the carbon produced from the interaction of Fe with the various CO/H_2 mixtures revealed that graphite nanofibers were the exclusive form of resulting products. High-resolution examination of the products showed that the graphite sheets constituting these nanofibers were aligned in a direction substantially perpendicular to the longitudinal axis of the fibers in the so-called "platelet" arrangement. It is evident that the selection of the specific catalyst, the reaction temperature and the presence of hydrogen in the CO-containing reactant mixture play critical roles with regard to determining the degree of crystallinity, the arrangement of the graphite sheets and the overall structure of the nanofibers.

Fe and supported Fe with $CO/C_2H_4/H_2$

When Fe powder was heated in $CO/C_2H_4/H_2$ mixtures at temperatures between 500 and 1100°C it was observed that substantially straight carbon nanofibers were produced. Examination by high-resolution TEM revealed that this catalyst system generated a nanofiber structure in which the graphite sheets were aligned in a direction perpendicular longitudinal axis of the fiber, in a so-called "platelet" arrangement.

In contrast, when the Fe particles were supported on graphite, silica or γ-alumina these systems heated in $CO/C_2H_4/H_2$ mixtures at temperatures between 500 and 1100°C once again the nanofibers were substantially straight. In this case, however, high-resolution TEM examination showed that the detailed structure of the nanofibers was one in which the graphite sheets were aligned in a direction substantially parallel to the fiber growth axis. Furthermore, these examinations showed that the nanofibers were cylindrical in cross-section and possessed continuous layers of ordered carbon atoms and a distinct inner core region. The characteristics of these nanofibers were identical to those claimed by Tennent (US 4,663,230).

The characteristics described above for nanofibers produced from $CO/C_2H_4/H_2$ mixtures over supported iron catalysts are quite different to those described in the present application. In this case, while the graphite platelets are substantially parallel to the fiber growth axis, they are in the form of non-continuous sheets and the cross-section of the nanofiber is faceted and as such, non-cylindrical in outline.

I hereby declare that all statements made herein are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Date April 9, 2004

R. Terry K. Baker